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(54) **Polymerization catalyst.**

(57) **An olefin polymerization catalyst comprises the reaction product of a metallocene complex of Group IVB, VB, VIB, and VIII of the Periodic Table and an excess of alumoxane.**

1 This invention relates to a new composition of matter which
2 is useful as a catalyst for the polymerization and copolymerization of
3 olefins and particularly useful for the polymerization of ethylene and
4 copolymerization of ethylene with 1-olefins having 3 or more carbon
5 atoms such as, for example, propylene, i-butene, 1-butene, 1-pentene,
6 1-hexene, and 1-octene; dienes such as butadiene, 1,7-octadiene, and
7 1,4-hexadiene or cyclic olefins such as norbornene. The invention
8 particularly relates to a new transition metal containing composition
9 of matter which can be employed as an olefin polymerization catalyst
10 without the use of an organometallic cocatalyst. The invention
11 further generally relates to the method of preparing the new compo-
12 sition of matter and to a process for polymerization of ethylene alone
13 or with other 1-olefins or diolefins in the presence of the new tran-
14 sition metal containing catalyst comprising the reaction product of a
15 metallocene and an alumoxane.

16 Traditionally, ethylene and 1-olefins have been polymerized
17 or copolymerized in the presence of hydrocarbon insoluble catalyst
18 systems comprising a transition metal compound and an aluminum alkyl.
19 More recently, active homogeneous catalyst systems comprising a bis-
20 (cyclopentadienyl)titanium dialkyl or a bis(cyclopentadienyl)zir-
21 conium dialkyl, an aluminum trialkyl and water have been found to be
22 useful for the polymerization of ethylene. Such catalyst systems are
23 generally referred to as "Ziegler-type catalysts".

24 German Patent Application 2,608,863 discloses the use of a
25 catalyst system for the polymerization of ethylene consisting of bis
26 (cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water.

27 German Patent Application 2,608,933 discloses an ethylene
28 polymerization catalyst system consisting of zirconium metallocenes of
29 the general formula $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$, wherein n
30 stands for a number in the range of 1 to 4, Y for R, CH_2AlR_2 ,
31 $\text{CH}_2\text{CH}_2\text{AlR}_2$ and $\text{CH}_2\text{CH}(\text{AlR}_2)_2$, wherein R stands for alkyl or metallo alkyl,
32 and an aluminum trialkyl cocatalyst and water.

33 European Patent Application No. 0035242 discloses a process
34 for preparing ethylene and atactic propylene polymers in the presence
35 of a halogen-free Ziegler catalyst system of (1) cyclopentadienyl

1 compound of the formula $(\text{cyclopentadienyl})_n \text{MeY}_{4-n}$ in which n is an
2 integer from 1 to 4, Me is a transition metal, especially zirconium,
3 and Y is either hydrogen, a $\text{C}_1\text{-C}_5$ alkyl or metallo alkyl group or
4 a radical having the following general formula CH_2AIR_2 , $\text{CH}_2\text{CH}_2\text{AIR}_2$ and
5 $\text{CH}_2\text{CH}(\text{AIR}_2)_2$ in which R represents a $\text{C}_1\text{-C}_5$ alkyl or metallo alkyl
6 group, and (2) an alumoxane.

7 Additional teachings of homogeneous catalyst systems
8 comprising a metallocene and alumoxane are European Patent Application
9 0069951 of Kaminsky et al, U.S. 4,404,344 issued September 13, 1983 of
10 Sinn et al., and U.S. Applications 697,308 filed February 1, 1985,
11 501,588 filed May 27, 1983, 728,111 filed April 29, 1985 and 501,740
12 filed June 6, 1983, each commonly assigned to Exxon Research and
13 Engineering Company.

14 An advantage of the homogeneous catalyst system comprising a
15 metallocene and an alumoxane is the very high activity obtained for
16 ethylene polymerization. Another significant advantage is, unlike
17 olefin polymers produced in the presence of conventional heterogeneous
18 Ziegler catalysts, terminal unsaturation is present in polymers pro-
19 duced in the presence of these homogeneous catalysts. Nevertheless,
20 the catalysts suffer from a disadvantage, that is, the ratio of
21 alumoxane to metallocene is high, for example in the order of 1,000 to
22 1 up to as high as $10^6:1$. Such voluminous amounts of alumoxane
23 would require extensive treatment of obtained polymer product in order
24 to remove the undesirable aluminum. A second disadvantage of the
25 homogeneous catalyst system, which is also associated with traditional
26 heterogeneous Ziegler catalysts, is the multiple of delivery systems
27 required for introducing the individual catalyst components into the
28 polymerization reactor. A third disadvantage is the high costs of the
29 alumoxane.

30 It would be highly desirable to provide a metallocene based
31 catalyst which is commercially useful for the polymerization of ole-
32 fins wherein the aluminum to transition metal ratio is within respect-
33 able ranges and further to provide a polymerization catalyst which
34 does not require the presence of a cocatalyst thereby reducing the
35 number of delivery systems for introducing catalyst into polymeri-
36 zation reactor.

1 In accordance with the present invention, a new composition
2 of matter comprising a metallocene-alumoxane reaction product is
3 provided which is useful as a catalyst for olefin polymerization and
4 particularly useful for the production of low, medium and high density
5 polyethylenes and copolymers of ethylene with alphaolefins having 3 to
6 18 or more carbon atoms and/or diolefins having up to 18 carbon atoms
7 or more.

8 The new composition of matter provided in accordance with one
9 embodiment of this invention, comprises the reaction product of at
10 least one metallocene and an excess of alumoxane thereby providing a
11 metallocene-alumoxane reaction product. In accordance with another
12 embodiment of this invention, a metallocene-alumoxane catalyst which
13 can be usefully employed is provided as the sole catalyst component in
14 an olefin polymerization process.

15 The reaction product will polymerize olefins at commercially
16 respectable rates without the presence of the objectionable excess of
17 alumoxane as required in the homogenous system.

18 In yet another embodiment of this invention there is provided
19 a process for the polymerization of ethylene and other olefins, and
20 particularly homopolymers of ethylene and copolymers of ethylene and
21 higher alpha-olefins and/or diolefins and/or cyclic olefins such as
22 norbornene in the presence of the new catalysts.

23 The metallocenes employed in the production of the reaction
24 product are organometallic compounds which are cyclopentadienyl deri-
25 vatives of a Group IVB, VB, VIB or VIII metal of the Periodic Table
26 (66th Edition of Handbook of Chemistry and Physics, CRC Press
27 [1985-86] CAS version) and include mono, di and tricyclopentadienyls
28 and their derivatives of the transition metals. Particularly desi-
29 rable are metallocene complexes of a Group IVB and VB metal such as
30 titanium, zirconium, hafnium and vanadium. The alumoxanes employed in
31 forming the reaction product with the metallocenes are themselves the
32 reaction products of an aluminum trialkyl with water.

33 The alumoxanes are well known in the art and comprise oligo-
34 meric linear and/or cyclic alkyl alumoxanes represented by the formula:

1 (I) $R-(Al-O)_n-AlR_2$ for oligomeric, linear alumoxanes and
 2 |
 3 R

4 (II) $(-Al-O)_m$ for oligomeric, cyclic alumoxane.
 5 |
 6 R

7 wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R
 8 is a C_1-C_8 alkyl group and preferably methyl. Generally, in the
 9 preparation of alumoxanes from, for example, aluminum trimethyl and
 10 water, a mixture of linear and cyclic compounds is obtained.

11 The alumoxanes can be prepared in a variety of ways. Prefer-
 12 ably, they are prepared by contacting water with a solution of alumi-
 13 num trialkyl, such as, for example, aluminum trimethyl, in a suitable
 14 organic solvent such as benzene or an aliphatic hydrocarbon. For
 15 example, the aluminum alkyl is treated with water in the form of a
 16 moist solvent. In a preferred method, the aluminum alkyl, such as
 17 aluminum trimethyl, can be desirably contacted with a hydrated salt
 18 such as hydrated ferrous sulfate. The method comprises treating a
 19 dilute solution of aluminum trimethyl in, for example, toluene with
 20 ferrous sulfate heptahydrate.

21 PREFERRED EMBODIMENTS

22 Briefly, the new transition metal containing composition of
 23 matter of the present invention is obtained by reacting an excess of
 24 alumoxane with at least one metallocene in the presence of a suitable
 25 solvent. The reaction product can be employed as the sole catalyst
 26 component for the polymerization of olefins or it can be employed in
 27 combination with other catalyst systems such as, for example, titanium
 28 halide-aluminum alkyl catalyst system.

29 The normally hydrocarbon soluble metallocenes and alumoxanes
 30 are converted to a relatively hydrocarbon insoluble solid reaction
 31 product by contacting said metallocenes and alumoxanes in a suitable
 32 solvent. The order of addition in contacting the metallocene and
 33 alumoxane can vary. For example, the metallocene (neat or dissolved
 34 in a suitable solvent) can be first added to the reaction vessel
 35 followed by the addition thereto of the alumoxane; the alumoxane and
 36 metallocene can be added to the reaction vessel simultaneously; the

1 alumoxane can be first added to the reaction vessel followed by the
2 addition of the metallocene. In accordance with the preferred embodi-
3 ment of this invention the metallocene dissolved in a suitable inert
4 hydrocarbon solvent is added to a stirred solution of the alumoxane.

5 The preparation of the metallocene-alumoxane reaction
6 product, as mentioned above, is conducted in an inert solvent, prefer-
7 ably a hydrocarbon solvent in which the metallocene and alumoxane are
8 soluble. Preferred solvents include mineral oils and the various
9 hydrocarbons which are liquid at reaction temperatures and in which
10 the individual ingredients are soluble. Illustrative examples of
11 useful solvents include the alkanes such as pentane, iso-pentane,
12 hexane, heptane, octane, nonane, and the like; cycloalkanes such as
13 cyclopentane, cyclohexane, and the like; and aromatics such as ben-
14 zene, toluene, ethylbenzene, diethylbenzene, and the like.

15 The solid catalyst prepared in accordance with this invention
16 is generally sparingly soluble at ambient temperatures in aromatic
17 solvents, insoluble in aliphatic solvents and decomposes in polar
18 solvents.

19 Preferably, the metallocene is dissolved in a hydrocarbon in
20 which the reaction product of the alumoxane and metallocene is largely
21 insoluble such as pentane. The amount of solvent to be employed can
22 vary over a wide range without a deleterious effect of the reaction.
23 In accordance with the preferred embodiment of this invention, the
24 amount of solvent to be employed is enough to completely dissolve the
25 metallocene and alumoxane independently prior to addition.

26 The metallocene and alumoxane can be added to the reaction
27 vessel rapidly or slowly. The temperature maintained during the
28 contact of the reactants can vary widely, such as, for example, from
29 about -78°C to about 50°C. Greater or lesser temperatures can also be
30 employed. Preferably, the alumoxanes and metallocenes are contacted
31 at 0°C temperature. The reaction between the alumoxane and the metal-
32 locene is rapid, and hence the reaction between the alumoxane and the
33 metallocene is maintained for about 2 to 60 minutes. Preferably, the
34 reaction is maintained for about 15 minutes at subambient tempera-
35 tures. The reaction of the alumoxane and the metallocene is evidenced
36 by the color change and formation of a precipitate or oil.

1 At all times, the individual ingredients as well as the
2 recovered catalyst are protected from oxygen and moisture. Therefore,
3 the reactions must be performed in an oxygen and moisture free
4 atmosphere and recovered in an oxygen and moisture free atmosphere.
5 Preferably, therefore, the reaction is performed in the presence of an
6 inert dry gas such as, for example, helium or nitrogen. The recovered
7 solid catalyst can be maintained in a nitrogen atmosphere, preferably
8 a subambient temperature.

9 The reaction products of the metallocene and alumoxane which
10 are generally solid materials when produced in aliphatic solvents and
11 oils when produced in aromatic solvents can be recovered by any well-
12 known technique. For example, the solid material can be recovered
13 from the liquid by vacuum filtration or decantation. The oils can be
14 recovered by decantation, and when dried, became glassy solids. The
15 recovered material is thereafter dried under a stream of pure dry
16 nitrogen, dried under vacuum, or by any other convenient manner. The
17 recovered solid is a catalytically active material.

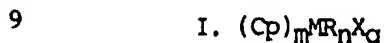
18 The solid can be usefully employed in gas phase polymeri-
19 zation, slurry polymerization, or in solution polymerization.

20 The amount of alumoxane and metallocene usefully employed in
21 preparation of the solid catalyst component can vary over a wide
22 range. To obtain a stable solid the mole ratio of alumoxane to metal-
23 locene is ideally greater than 12:1, preferably about 12:1 to about
24 100:1. Ratios in the range of 20-40:1 are desirable, however, the
25 greater amounts can be usefully employed. The solid obtained will
26 have an aluminum to transition metal ratio in the range of about 12 to
27 100 moles of aluminum per mole of metal and preferably 12 to 30 moles
28 of aluminum per mole of metal. The solid so obtained has excellent
29 catalytic activity with respect to olefin polymerization while
30 employing significantly lower ratios of aluminum to transition metal
31 as compared to the homogeneous systems, whereby polymerization is
32 carried out by adding the alumoxane and metallocene independently to
33 the reactor.

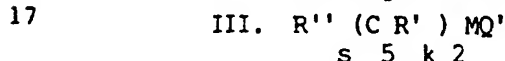
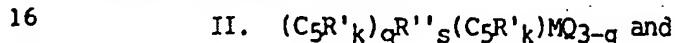
34 The present invention employs at least one metallocene
35 compound in the formation of the solid catalyst. Metallocene, i.e. a
36 cyclopentadienylide, is a metal derivative of a cyclopentadiene. The
37 metallocenes usefully employed in accordance with this invention
38 contain at least one cyclopentadiene ring. The metal is selected from

1 Group IVB, VB, VIB, and VIII metal, preferably IVB and VB metal,
2 preferably titanium, zirconium, hafnium, chromium, and vanadium, and
3 especially titanium and zirconium. The cyclopentadienyl ring can be
4 unsubstituted or contain substituents such as, for example, a hydro-
5 carbyl substituent. The metallocene can contain one, two, or three
6 cyclopentadienyl rings however two rings are preferred.

7 The preferred metallocenes can be represented by the general
8 formulas:



10 wherein Cp is a cyclopentadienyl ring, M is a Group IVB, VB, VIB, or
11 VIII transition metal, R is a hydride or a hydrocarbyl group or
12 hydrocarboxy having from 1 to 20 carbon atoms, X is a halogen, and m =
13 1-3, n = 0-3, q = 0-3 and the sum of m+n+q is equal to the oxidation
14 state of the metal. The metal is most preferably in its highest
15 formal oxidation state.



18 wherein $(C_5R'_k)$ is a cyclopentadienyl or substituted cyclopenta-
19 dienyl, each R' is the same or different and is hydrogen or a hydro-
20 carbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl
21 radical containing from 1 to 20 carbon atoms or two carbon atoms are
22 joined together to form a C₄-C₆ ring, R'' is a C₁-C₄ alkylene radical,
23 a dialkyl germanium or silicon, or a alkyl phosphine or amine radical
24 bridging two $(C_5R'_k)$ rings, Q is a hydrocarbyl radical such as aryl,
25 alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20
26 carbon atoms, hydrocarboxy radical having from 1-20 carbon atoms or
27 halogen and can be the same or different from each other, Q' is an
28 alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or
29 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1 and k is 5
30 when s is 0, and M is as defined above.

31 Exemplary hydrocarbyl radicals are methyl, ethyl, propyl,
32 butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl,
33 cetyl, 2-ethylhexyl, phenyl and the like.

34 Exemplary halogen atoms include chlorine, bromine, fluorine
35 and iodine and of these halogen atoms, chlorine is preferred.

36 Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy,
37 butoxy, amyloxy and the like.

1 Exemplary of the alkylidene radicals is methylenidene, ethyl-
2 idene and propylenidene.

3 Illustrative, but non-limiting examples of the metallocenes
4 represented by formula I are dialkyl metallocenes such as bis(cyclo-
5 pentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl,
6 bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium
7 diphenyl, bis(cyclopentadienyl)hafnium dimethyl and diphenyl,
8 bis(cyclopentadienyl)titanium di-neopentyl, bis(cyclopentadienyl)-
9 zirconium di-neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis-
10 (cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium
11 dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)-
12 titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl
13 chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclo-
14 pentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium
15 ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis-
16 (cyclopentadienyl)titanium methyl bromide, bis(cyclopentadienyl)methyl
17 iodide, bis(cyclopentadienyl)titanium ethyl bromide, bis(cyclopenta-
18 dienyl)titanium ethyl iodide, bis(cyclopentadienyl)titanium phenyl
19 bromide, bis(cyclopentadienyl)titanium phenyl iodide, bis(cyclopenta-
20 dienyl)zirconium methyl bromide, bis(cyclopentadienyl)zirconium methyl
21 iodide, bis(cyclopentadienyl)zirconium ethyl bromide, bis(cyclopenta-
22 dienyl)zirconium ethyl iodide, bis(cyclopentadienyl)zirconium phenyl
23 bromide, bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl
24 metallocenes such as cyclopentadienyltitanium trimethyl, cyclopenta-
25 dienyl zirconium triphenyl, and cyclopentadienyl zirconium trineo-
26 pentyl, cyclopentadienylzirconium trimethyl, cyclopentadienylhafnium
27 triphenyl, cyclopentadienylhafnium trineopentyl, and cyclopentadienyl-
28 hafnium trimethyl.

29 Illustrative, but non-limiting examples of II and III metal-
30 locenes which can be usefully employed in accordance with this
31 invention are monocyclopentadienyls titanocenes such as, pentamethyl-
32 cyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl
33 titanium trichloride; bis(pentamethylcyclopentadienyl) titanium
34 diphenyl, the carbene represented by the formula
35 $\text{bis(cyclopentadienyl)titanium=CH}_2$ and derivatives of this reagent
36 such as $\text{bis(cyclopentadienyl)Ti=CH}_2 \cdot \text{Al(CH}_3)_3$, $(\text{Cp}_2\text{TiCH}_2)_2$,
37 $\text{Cp}_2\text{TiCH}_2\text{CH(CH}_3)_2$, $\text{Cp}_2\text{Ti-CHCH}_2\text{CH}_2$; substituted
38 bis(cyclopentadienyl)titanium (IV) compounds such as:

1 bis(indenyl)titanium diphenyl or dichloride, bis-
 2 (methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl, tri-
 3 alkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds
 4 such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or
 5 dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or
 6 dichloride and other dihalide complexes; silicon, phosphine, amine or
 7 carbon bridged cyclopentadiene complexes, such as dimethyl silyldi-
 8 cyclopentadienyl titanium diphenyl or dichloride, methyl phosphine
 9 dicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclo-
 10 pentadienyl titanium diphenyl or dichloride and other dihalide
 11 complexes and the like.

12 Illustrative but non-limiting examples of the zirconocenes
 13 Formula II and III which can be usefully employed in accordance with
 14 this invention are, pentamethylcyclopentadienyl zirconium trichloride,
 15 pentaethylcyclopentadienyl zirconium trichloride, bis(pentamethyl-
 16 cyclopentadienyl)zirconium diphenyl, the alkyl substituted cyclopenta-
 17 dienes, such as bis(ethyl cyclopentadienyl)zirconium dimethyl, bis(β-
 18 phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopenta-
 19 dienyl)zirconium dimethyl, bis(n-butyl-cyclopentadienyl)zirconium
 20 dimethyl, bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl,
 21 bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and haloalkyl and
 22 dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and
 23 penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl)
 24 zirconium di-methyl, bis(1,2-dimethylcyclopentadienyl)zirconium
 25 dimethyl and dihalide complexes of the above; silicone, phosphorus,
 26 and carbon bridged cyclopentadiene complexes such as dimethylsilyldi-
 27 cyclopentadienyl zirconium dimethyl or dihalide, and methylene
 28 dicyclopentadienyl zirconium dimethyl or dihalide, and methylene
 29 dicyclopentadienyl zirconium dimethyl or dihalide, carbenes
 30 represented by the formula $Cp_2Zr=CHP(C_6H_5)_2CH_3$, and derivatives of these
 31 compounds such as $Cp_2ZrCH_2CH(CH_3)CH_2$.

32 Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopenta-
 33 dienyl)hafnium dimethyl, bis(cyclopentadienyl)vanadium dichloride and
 34 the like are illustrative of other metallocenes.

35 The polymerization may be conducted by a solution, slurry, or
 36 gas-phase technique, generally at a temperature in the range of about
 37 0°-160°C or even higher, and under atmospheric, subatmospheric, or
 38 superatmospheric pressure conditions; and conventional polymerization

1 adjuvants, such as hydrogen may be employed if desired. It is
2 generally preferred to use the catalyst compositions at a concen-
3 tration such as to provide about 0.00005 - 0.01%, most preferably
4 about 0.005 - 0.001%, by weight of transition metal (100 g
5 metal·g⁻¹ diluent).

6 A slurry polymerization process can utilize sub- or super-
7 atmospheric pressures and temperatures in the range of 40-110°C. In a
8 slurry polymerization, a suspension of solid, particulate polymer is
9 formed in a liquid polymerization medium to which ethylene, alpha-
10 olefin comonomer, hydrogen and catalyst are added. The liquid
11 employed as the polymerization medium can be an alkane or cycloalkane,
12 such as butane, pentane, hexane, or cyclohexane, or an aromatic hydro-
13 carbon, such as toluene, ethylbenzene or xylene. The medium employed
14 should be liquid under the conditions of the polymerization and rela-
15 tively inert. Preferably, hexane or toluene is employed.

16 In a slurry phase polymerization, the alkyl aluminum scaven-
17 ger is preferably dissolved in a suitable solvent, typically in an
18 inert hydrocarbon solvent such as toluene, xylene, and the like in a
19 molar concentration of about 1×10^{-3} M. However, greater or lesser
20 amounts can be used.

21 A gas-phase polymerization process utilizes superatmospheric
22 pressure and temperatures in the range of about 50°-120°C. Gas-phase
23 polymerization can be performed in a stirred or fluidized bed of cata-
24 lyst and product particles in a pressure vessel adapted to permit the
25 separation of product particles from unreacted gases. Thermostated
26 ethylene, comonomer, hydrogen and an inert diluent gas such as nitro-
27 gen can be introduced or recirculated so as to maintain the particles
28 at a temperature of 50°-120°C. Trimethylaluminum may be added as
29 needed as a scavenger of water, oxygen, and other adventitious impuri-
30 ties. Polymer product can be withdrawn continuously or semi-
31 continuing at a rate such as to maintain a constant product inventory
32 in the reactor. After polymerization and deactivation of the cata-
33 lyst, the product polymer can be recovered by any suitable means. In
34 commercial practice, the polymer product can be recovered directly
35 from the gas phase reactor, freed of residual monomer with a nitrogen
36 purge, and used without further deactivation or catalyst removal. The
37 polymer obtained can be extruded into water and cut into pellets or

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1 other suitable comminuted shapes. Pigments, antioxidants and other
2 additives, as is known in the art, may be added to the polymer.

3 The molecular weight of polymer product obtained in accordance with this invention can vary over a wide range, such as low as
4 500 up to 2,000,000 or higher and preferably 1,000 to about 500,000.

5
6 For the production of polymer product having a narrow molecular weight distribution, it is preferable to employ only one metallocene in forming the solid catalyst with the alumoxane. For broad
7 molecular weight distribution or broad compositional distribution
8 polymer one employs two or more metallocenes in forming the solid
9 catalyst.

10
11 It is highly desirable to have for many applications, such as
12 extrusion and molding processes, polyethylenes which have a broad
13 molecular weight distribution of the unimodal and/or the multimodal
14 type. Such polyethylenes evidence excellent processability, i.e. they
15 can be processed at a faster throughput rate with lower energy
16 requirements and at the same time such polymers would evidence reduced
17 melt flow perturbations. Such polyethylenes can be obtained by providing a catalyst component comprising at least two different metallocenes, each having different propagation and termination rate
18 constants for ethylene polymerizations. Such rate constants are
19 readily determined by one of ordinary skill in the art.

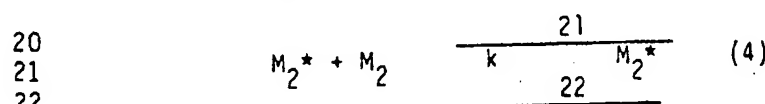
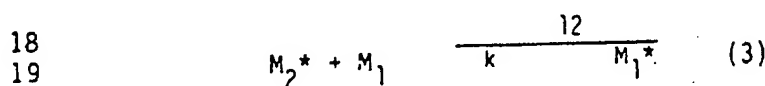
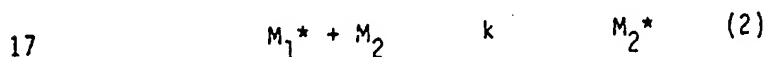
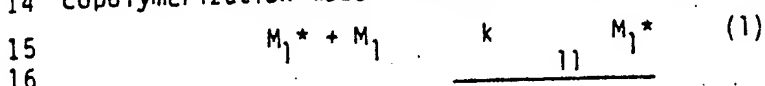
20
21 The molar ratio of the metallocenes, such as, for example, of
22 a zirconocene to a titanocene in such catalysts, can vary over a wide
23 range, and in accordance with this invention, the only limitation on
24 the molar ratios is the breadth of the Mw distribution or the degree
25 of bimodality desired in the product polymer. Desirably, the metallocene to metallocene molar ratio will be about 1:1 to about 100:1,
26 and preferably 1:1 to about 10:1.

27
28 The present invention also provides a process for producing
29 (co)polyolefin reactor blends comprising polyethylene and copolyethylene-alpha-olefins. The reactor blends are obtained directly
30 during a single polymerization process, i.e., the blends of this
31 invention are obtained in a single reactor by simultaneously polymerizing ethylene and copolymerizing ethylene with an alpha-olefin
32 thereby eliminating expensive blending operations. The process of
33 producing reactor blends in accordance with this invention can be
34 employed in conjunction with other prior art blending techniques, for

1 example, the reactor blends produced in a first reactor can be sub-
2 jected to further blending in a second stage by use of the series
3 reactors.

4 In order to produce reactor blends the catalyst comprises at
5 least two different metallocenes each having different comonomer
6 reactivity ratios.

7 The comonomer reactivity ratios of the metallocenes in
8 general are obtained by well known methods, such as for example, as
9 described in "Linear Method for Determining Monomer Reactivity Ratios
10 in Copolymerization", M. Fineman and S. D. Ross, J. Polymer Science 5,
11 259 (1950) or "Copolymerization", F. R. Mayo and C. Walling, Chem.
12 Rev. 46, 191 (1950) incorporated herein in its entirety by reference.
13 For example, to determine reactivity ratios the most widely used
14 copolymerization model is based on the following equations:



23 where M_i refers to a monomer molecule which is arbitrarily desig-
24 nated i (where $i = 1, 2$) and M_i^* refers to a growing polymer chain
25 to which monomer i has most recently attached.

26 The k_{ij} values are the rate constants for the indicated
27 reactions. In this case, k_{11} represents the rate at which an
28 ethylene unit inserts into a growing polymer chain in which the
29 previously inserted monomer unit was also ethylene. The reactivity
30 rates follow as: $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$
31 wherein k_{11} , k_{12} , k_{22} and k_{21} are the rate constants for
32 ethylene (1) or comonomer (2) addition to a catalyst site where the
33 last polymerized monomer is ethylene (k_{1x}) or comonomer (2) (k_{2x}).

34 Since, in accordance with this invention, one can produce high
35 viscosity polymer product at a relatively high temperature, tempera-
36 ture does not constitute a limiting parameter as with the prior art
37 metallocene/alumoxane catalyst. The catalyst systems described
38 herein, therefore, are suitable for the polymerization of olefins in

1 solution, slurry or gas phase polymerizations and over a wide range of
2 temperatures and pressures. For example, such temperatures may be in
3 the range of about -60°C to about 280°C and especially in the range of
4 about 0°C to about 160°C. The pressures employed in the process of
5 the present invention are those well known, for example, in the range
6 of about 1 to 500 atmospheres, however, higher pressures can be
7 employed.

8 The polymers produced by the process of this present inven-
9 tion are capable of being fabricated into a wide variety of articles,
10 as is known for homopolymers of ethylene and copolymers of ethylene
11 and higher alpha-olefins. The present invention is illustrated by the
12 following examples.

13 Examples

14 In the Examples following the elemental analysis was obtained
15 through inductively coupled plasma emission spectroscopy on a Jarrell
16 Ash Spectrometer Model 750 manufactured by Jarrell Ash.

17 Bis(pentamethylcyclopentadienyl)zirconium bis-triflate was
18 manufactured by dissolving 2 grams of bis(pentamethylcyclopenta-
19 dienyl)zirconium dimethyl in 100 ml of toluene and cooling to -30°C.
20 To the cooled solution was added 1.53 grams of triflic acid
21 ($\text{CF}_3\text{SO}_3\text{H}$). The reaction was stirred for one hour and the solid
22 was isolated by filtration. The crude product was recrystallized from
23 dichloromethane and diethyl ether yielding 2.8 grams of yellow prisms
24 characterized by NMR spectroscopy (Varian XL200) to be bis-penta-
25 methylcyclopentadienyl-zirconium-bis-triflate. 1.0 grams of the
26 recovered complex was suspended in 50 ml of toluene under constant
27 stirring to which was added 0.11 g of trimethylaluminum. The solid
28 reaction product began immediately to dissolve. Reaction was
29 continued for 30 minutes, upon which the solvent was removed in
30 vacuo. The recovered product was recrystallized from toluene-pentane
31 to yield 0.80 grams of yellow crystals characterized by proton and
32 carbon NMR spectroscopy (Varian XL200) to be bis-pentamethylcyclo-
33 pentadienyl-zirconium-methyl-triflate.

34 The alumoxane employed was prepared by adding 76.5 grams
35 ferrous sulfate heptahydrate in 4 equally spaced increments over a 2
36 hour period to a rapidly stirred 2 liter round-bottom flask containing
37 1 liter of a 13.1 wt. % solution of trimethylaluminum (TMA) in
38 toluene. The flask was maintained at 50°C and under a nitrogen

1 atmosphere. Methane produced was continuously vented. Upon completion of the addition of ferrous sulfate heptahydrate the flask was continuously stirred and maintained at a temperature of 50°C for 6 hours. The reaction mixture was cooled to room temperature and was allowed to settle. The clear solution containing the alumoxane was separated by decantation from the insoluble solids.

7 In cases where the metallocene of interest is readily soluble in a saturated hydrocarbon such as pentane, it is desirable to have the methylalumoxane dissolved in that same solvent. Pentane solutions of alumoxane are prepared by concentrating a toluene solution of alumoxane (prepared as above) in vacuo to a clear viscous oil (i.e., where most of the toluene has been removed but prior to the point where a solid glass is formed). This oil is extracted with pentane to remove all pentane soluble aluminum components. The pentane solubles are separated from high molecular weight insoluble alumoxane oligomers by filtration, and analyzed for aluminum concentration by ICPEES.

17 Example 1

18 Catalyst Preparation

19 To a 0.5 liter reaction flask containing 1 gram of bis(pentamethylcyclopentadienyl)zirconium dichloride dissolved in 75 ml of toluene, there was added with constant stirring and at room temperature, 198 ml of a pentane solution 0.35 M in methylalumoxane. A reaction occurred immediately as evidenced by the formation of an insoluble yellow-oil. The reaction flask was cooled to -30°C and held at that temperature for one hour. The oil was separated from the mother liquor by decantation, washed with 30 ml of pentane and dried in vacuo yielding 1.47 grams of a glassy solid (Solid I). The aluminum:zirconium ratio was 33:1.

29 Polymerization

30 Solid I (0.05 g) was dissolved in 100 ml of toluene, injected into a 250 ml pressure reaction vessel and heated to 80°C. The vessel was pressured to 35 psi with ethylene and maintained for 20 minutes at 80°C with constant stirring. 4.4 grams of high-density polyethylene was isolated.

35 Example 2

36 Catalyst Preparation

37 To a .25 liter reaction flask containing 0.75 grams of bis(pentamethylcyclopentadienyl)zirconium dimethyl dissolved in 50 ml of

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1 toluene, there was added with constant stirring and at room tempera-
2 ture, 164 ml of a pentane solution 0.35 M in methylalumoxane. A
3 reaction occurred immediately, yielding a yellow oil. The reaction
4 flask was cooled to -30°C and held at that temperature for one hour.
5 The oil was separated from the mother liquor, washed with 50 ml of
6 pentane, and dried in vacuo, yielding 1.3 grams of a glassy solid
7 (Solid II). The aluminum:zirconium ratio was 32:1.

8 Polymerization

9 Solid II (0.05 g) was dissolved in 100 ml toluene, injected
10 into a 250 ml pressure reaction vessel and heated to 80°C . The vessel
11 was pressured to 35 psi with ethylene and maintained for 20 minutes at
12 80°C with constant stirring. 5.4 grams of high density polyethylene
13 was recovered.

14 Example 3

15 Catalyst Preparation

16 To a .25 liter reaction flask containing 1 gram of bis(n-
17 butylcyclopentadienyl)zirconium dichloride dissolved in 75 ml of a
18 20:80 mixture of toluene and pentane, there was added with constant
19 stirring, and at room temperature, 176 ml of methylalumoxane (0.35M).
20 The reaction vessel was cooled to -30°C and held at the temperature
21 for one hour. The oil was separated from the mother liquor by decan-
22 tation, washed with 20 ml of pentane, and dried in vacuo yielding 1.87
23 grams of a glassy solid (Solid III). The aluminum:zirconium ratio was
24 20:1.

25 Polymerization

26 Solid III (0.05 g) was dissolved in 100 ml toluene, injected
27 into a 250 ml reaction vessel and heated to 80°C . The vessel was
28 pressured to 35 psi with ethylene and maintained for 10 minutes at
29 80°C with constant stirring. 8.2 grams of high density polyethylene
30 was isolated.

31 Example 4

32 Catalyst Preparation

33 To a .25 liter reaction flask containing 0.50 grams of bis-
34 (cyclopentadienyl)titanium methyl chloride dissolved in 75 ml of
35 toluene, there was added with constant stirring and at room tempera-
36 ture, 156 ml of a pentane solution 0.35 M in methylalumoxane. A
37 chemical reaction occurred as evidenced by the immediate formation of
38 a deep red oil. The reaction vessel was cooled to -30°C and held at

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1 that temperature for a one hour period. The oil was separated from
2 the mother liquor by decantation, washed with 50 ml pentane, and dried
3 in vacuo, yielding 2.78 grams of a glassy solid (Solid IV). The
4 aluminum:titanium ratio was 20:1.

5 Polymerization

6 Solid IV (0.05 g) was dissolved in 100 ml toluene, injected
7 into a 250 ml pressure reaction vessel and heated to 80°C. The vessel
8 was pressured to 35 psi with ethylene and maintained for 20 minutes at
9 80°C with constant stirring. 3.8 grams of high density polyethylene
10 was isolated.

11 Example 5

12 Catalyst Preparation

13 To a 0.25 liter reaction flask containing 0.71 grams of bis-
14 (pentamethylcyclopentadienyl)zirconium-methyl-triflate dissolved in
15 100 ml of toluene, there was added, with constant stirring and at room
16 temperature, 97 ml of a pentane solution 0.35 M of methylalumoxane. A
17 reaction occurred immediately as evidenced by the formation of an
18 insoluble yellow oil. The reaction vessel was cooled to -30°C and
19 held at that temperature for one hour. The oil was separated from the
20 mother liquor by decantation, washed in 50 ml of pentane and dried in
21 vacuo, yielding 1.80 grams of a glassy solid (Solid V). The alumi-
22 num:zirconium ratio was 68:1.

23 Polymerization

24 Solid V (0.05 g) was dissolved in 100 ml of toluene, injected
25 into a 250 ml pressure reaction vessel and heated to 80°C. The vessel
26 was pressured to 35 psi with ethylene was maintained for 20 minutes at
27 80°C and with constant stirring. 3.2 grams of polyethylene was iso-
28 lated.

29 Example 6

30 Catalyst Preparation

31 To a 0.25 liter reaction flask containing 1 gram of bis-
32 (pentamethylcyclopentadienyl)titanium dichloride dissolved in 60 ml of
33 toluene there was added, with constant stirring and at room tempera-
34 ture, 80 ml of a pentane solution 0.79 M in methylalumoxane. A
35 reaction occurred immediately as evidenced by the formation of a
36 sparingly soluble deep red oil. The reaction vessel was cooled to
37 -30°C and held at that temperature for one hour. The oil was sepa-
38 rated from the mother liquor, washed in 50 ml of pentane and dried in

1 vacuo, yielding 1.95 grams of a glassy solid (Solid VI). The
2 aluminum:titanium ratio was 17:1.

3 Polymerization

4 Solid VI (0.05 g) was dissolved in 100 ml of toluene,
5 injected into a 250 ml pressure reaction vessel and heated to 80°C.
6 The vessel was pressured to 35 psi with ethylene and maintained for 20
7 minutes at 80°C with constant stirring. 0.9 gram of polyethylene was
8 isolated.

9 Example 7

10 Catalyst Preparation

11 To a .25 liter reaction flask containing 0.75 grams of bis(n-
12 butylcyclopentadienyl)titanium dichloride dissolved in 100 ml of an
13 80:20 mixture of pentane and toluene there was added, with constant
14 stirring and at room temperature, 66 ml of a pentane solution 0.35 M
15 in methylalumoxane. A reaction occurred immediately as evidenced by
16 the formation of an insoluble red oil. The reaction vessel was cooled
17 to -30°C and held at that temperature for one hour. The oil was
18 separated from the mother liquor, washed in 50 ml of pentane and dried
19 in vacuo, yielding 0.75 grams of a glassy solid (Solid VII). The
20 aluminum:titanium ratio was 24:1.

21 Polymerization

22 Solid VII (0.05 g) was dissolved in 100 ml of toluene,
23 injected into a 250 ml pressure reaction vessel and heated to 80°C.
24 The vessel was pressured to 35 psi with ethylene and maintained for 20
25 minutes at 80°C with stirring. 3.2 grams of high density polyethylene
26 was isolated.

27 Example 8

28 Catalyst Preparation

29 To a .25 liter reaction flask containing 1 gram of bis(cyclo-
30 pentadienyl)titanium diphenyl dissolved in 100 ml of an 80:20 mixture
31 of pentane and toluene there was added, with constant stirring and at
32 room temperature, 95 ml of a pentane solution 0.79 M in methylalum-
33 oxane. A reaction occurred immediately forming an insoluble oil. The
34 reaction vessel was cooled to -30°C and held at that temperature for
35 one hour. The oil was separated from the mother liquor, washed in 50
36 ml of pentane and dried in vacuo, yielding 0.70 grams of a glassy
37 solid (Solid VIII). The aluminum:titanium ratio was 17:1.

Polymerization

1 Solid VIII (0.05 g) was dissolved in 100 ml of toluene,
2 injected into a 250 ml pressure reaction vessel and heated to 80°C.
3 The vessel was pressured to 35 psi with ethylene and maintained for 20
4 minutes at 80°C with constant stirring. 2.9 grams of high density
5 polyethylene was isolated.
6

7 Example 9

8 Catalyst Preparation

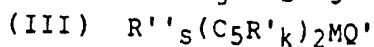
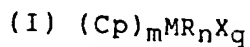
9 To a 0.25 liter reaction flask containing 0.5 grams of bis-
10 (cyclopentadienyl)zirconium dimethyl dissolved in 100 ml of a 90:10
11 mixture of pentane and toluene there was added, with constant stirring
12 and at room temperature, 63 ml of a pentane solution 0.79 M in methyl-
13 alumoxane. A reaction occurred immediately as evidenced by the forma-
14 tion of an off-white precipitate. The reaction vessel was cooled to
15 -30°C and held at that temperature for one hour. The precipitate was
16 collected by filtration, washed with 50 ml of pentane and dried in
17 vacuo, yielding 1.9 grams of a white solid (Solid IX). The
18 aluminum:zirconium ratio was 21.7:1.

19 Polymerization

20 Solid IX (0.05 g) was dissolved in 100 ml of toluene,
21 injected into a 250 ml pressure reaction vessel and heated to 80°C.
22 The vessel was pressured to 35 psi with ethylene and maintained for 10
23 minutes at 80°C with constant stirring. 7.2 grams of high density
24 polyethylene was isolated.

CLAIMS

1. An olefin polymerization catalyst comprising the reaction product of at least one metallocene of a transition metal of Group IVB, VB, VIB, and VIII of the Periodic Table (66th Edition of Handbook of Chemistry and Physics, CRC Press [1985-86] CAS version) and an excess of alumoxane.
2. A catalyst in accordance with claim 1 wherein the metallocene is selected from titanium, zirconium, hafnium and vanadium metallocenes and mixtures thereof.
3. A catalyst in accordance with claim 2 wherein the metallocene is selected from titanium and zirconium metallocenes and mixtures thereof.
4. A catalyst in accordance with any one of the preceding claims wherein the alumoxane is methyl alumoxane.
5. A catalyst in accordance with any one of the preceding claims wherein the molar ratio of aluminum to transition metal in the product is from 12:1 to 100:1.
6. A catalyst in accordance with claim 5 wherein the ratio is from 20:1 to 40:1.
7. A catalyst in accordance with any one of the preceding claims wherein the metallocene is represented by the formula



wherein Cp is a cyclopentadienyl ring, M is a Group IVB, VB, VIB, or VIII transition metal, R is hydride; a hydrocarbyl group or hydrocarboxy having from 1 to 20

carbon atoms, X is a halogen, $m=1-3$, $n=0-3$, $q=0-3$ and the sum of $m + n + q$ is equal to the oxidation state of M, $(C_5R'_k)$ is a cyclopentadienyl or a substituted cyclopentadienyl; each R' is the same or different and is hydrogen or a hydrocarbyl radical selected from alkyl, alkenyl, aryl, alkylaryl or arylalkyl radicals containing from 1 to 20 carbon atoms, or two carbon atoms are joined together to form a C_4-C_6 ring, R'' is a C_1-C_4 alkylene radical, a dialkylgermanium or silicon or an alkyl phosphine or amine radical bridging two $(C_5R'_k)$ rings; Q is a hydrocarbyl radical selected from aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radicals having from 1-20 carbon atoms, hydrocarboxy radical having from 1-20 carbon atoms or halogen and can be the same or different from each other; Q' is an alkylidene radical having from 1 to 20 carbon atoms; s is 0 or 1; g is 0, 1, or 2; s is 0 when g is 0; k is 4 when s is 1 and k is 5 when s is 0.

8. A catalyst in accordance with claim 7 wherein the metallocenes are selected from bis(cyclopentadienyl) zirconium dichloride, bis(cyclopentadienyl) zirconium methyl chloride, bis(cyclopentadienyl) zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium methyl chloride, bis(methylcyclopentadienyl)zirconium dimethyl, bis-(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)zirconium methyl chloride, bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl) zirconium dichloride, bis(n-butylcyclopentadienyl)zirconium methyl chloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl) titanium dichloride, bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)- titanium dimethyl, bis(methylcyclopentadienyl)titanium diphenyl, bis-(methylcyclopentadienyl) titanium dichloride, bis(methylcyclopentadienyl)titanium diphenyl,

bis(methylcyclopentadienyl)titanium methyl chloride,
bis(methylcyclopentadienyl)titanium dimethyl, bis(penta-
methylcyclopentadienyl)titanium dichloride,
bis(pentamethylcyclopenta- dienyl)titanium diphenyl,
bis(pentamethylcyclopentadienyl)titanium methyl chloride,
bis(pentamethylcyclopentadienyl)titanium dimethyl,
bis(n-butyl-cyclopentadienyl)titanium diphenyl,
bis(n-butyl-cyclo- pentadienyl)titanium dichloride and
mixtures thereof.

9. A method for preparing an olefin polymerization catalyst comprising at least one metallocene of a transition metal of Group IVB, VB, VIB and VIII of the Periodic Table and an alumoxane which comprises contacting at least one metallocene and an excess of alumoxane in an inert solvent.

10. The method in accordance with claim 9 wherein the molar ratio of the alumoxane contacted with the metallocene (based on aluminum and transition metal) is in the range of 12:1 to 100:1.

11. A process for producing polymers of ethylene or copoly- mers of ethylene and alpha olefins or diolefins which process comprises polymerizing the monomers in the presence of a catalyst according to any one of claims 1 to 8 or prepared by the method of claim 9 or 10.

12. A process according to claim 11 wherein said catalyst is employed in an amount such as to provide from 0.00005-0.01 wt % of transition metal.

13. A process according to claim 11 or 12 wherein the nature of the catalyst and the polymerization conditions are adjusted to control the nature of the polymer or copolymer product.

14. A process according to claim 11, 12 or 13 wherein said catalyst is the sole catalyst component of the polymerization reaction.



EP. 86 30 9683

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, X	EP-A-0 128 046 (EXXON) * Claims; page 7, line 35 - page 8, line 3 * -----	1-14	C 08 F 10/00 C 08 F 4/64
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 11-02-1987	Examiner DE ROECK R.G.
CATEGORY OF CITED DOCUMENTS			
X : particular document relevant if taken alone Y : particular document relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	